Effects of Impurities with Singlet-Triplet Configuration on Multiband Superconductors

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Roles of multipole degrees of freedom in multiband superconductors are investigated in a case of impurities whose low-lying states consist of singlet ground and triplet excited states, which is related to the experimental fact that the transition temperature $T_{\rm c}$ is increased by Pr substitution for La in $LaOs_4Sb_{12}$. The most important contribution to the $T_{\rm c}$ increase comes from the inelastic interband scattering of electrons coupled to quadrupole or octupole moments of impurities. It is found that a magnetic field modifies an effective pairing interaction and the scattering anisotropy appears in the field-orientation dependence of the upper critical field $H_{\rm c2}$ in the vicinity of $T_{\rm c}$, although a uniaxial anisotropic field is required for experimental detection. This would be proof that the Pr internal degrees of freedom are relevant to the stability of superconductivity in $(La_{1-x}Pr_x)Os_4Sb_{12}$.

KEYWORDS: heavy fermion, skutterudite, impurity, crystal field, multiband superconductivity

1. Introduction

It is common knowledge that magnetic impurities induce pair breaking and a decrease in superconducting transition temperature $T_{\rm c}$. In a multiband case, however, there is room to reconsider such a conventional understanding.[1,2] Electron scattering by impurities occurs not only within one band (intraband) but also between different bands (interband). In addition, variations in order parameters can be considered for superconducting bands. In a two-band case, for instance, the $s_{\pm}$-wave state is characterized by the sign-reversing order parameters.[3,4] According to recent studies on the $s_{\pm}$-wave state, interband scattering does not contribute to $T_{\rm c}$ suppression for magnetic impurities.[5,6] This behavior resembles that of intraband scattering by nonmagnetic impurities in a single-band s-wave superconductor. Furthermore, $T_{\rm c}$ can be increased by inelastic interband scattering if the impurities have such internal degrees of freedom as crystal-field split energy levels.[7] The idea was originally proposed by Fulde *et al.* for nonmagnetic impurities in a single-band superconductor;[8] however, it has been considered that magnetic impurities always induce $T_{\rm c}$ suppression. We have to check carefully the potential roles of impurities with orbital degrees of freedom, e.g., multipoles in f-electron systems.

Since the discovery of the heavy fermion superconductor $PrOs_4Sb_{12}$ ($T_{\rm c} = 1.85$ K),[9] much attention has been attracted by the following unique superconducting properties:[10] (1) Change in gap symmetry in a magnetic field. This was first observed as the field orientation dependence of oscillating patterns on thermal conductivity,[11] although no symptom of cubic symmetry breaking was found in a recent angle-resolved specific heat experiment.[12] (2) Broken time reversal symmetry below $T_{\rm c}$. An internal magnetic field emerges spontaneously but is extremely small, which was detected by muon spin relaxation measurement.[13] The identification of the pairing parity is under debate. (3) Robustness against substitution effects. Substituting La for Pr leads to the gradual decrease in $T_{\rm c}$.[14] Surprisingly, the x dependence of $T_{\rm c}$ in $(Pr_{1-x}La_x)Os_4Sb_{12}$ is smoothly connected to the $T_{\rm c}(= 0.74$ K) of $LaOs_4Sb_{12}$ that exhibits the conventional s-wave property.[14,15] In another experiment on $Pr(Os_{1-x}Ru_x)_4Sb_{12}$, $T_{\rm c}$ gradually decreases until $x \sim 0.6$ and then shows a monotonic increase up to the $T_{\rm c}(= 1.3$ K) of $PrRu_4Sb_{12}$, which is also an s-wave superconductor.[16] It has been considered that these unconventional properties are associated with the Pr $4f$-electron behavior, although this association is still mysterious.

It is also important to note that $PrOs_4Sb_{12}$ exhibits the quadrupole ordering in a higher magnetic field where the superconductivity disappears.[10,17,18] This ordering phase diagram is successfully explained by the localized Pr $4f^2$ quasi-quartet model.[19,20] In fact, it has been established by the recent experiments that the Pr low-lying states consist of Γ_1 singlet ground and $\Gamma_4^{(2)}$ excited triplet states well separated from the higher crystal-field energy levels.[21,22] The $\Gamma_4^{(2)}$ representation is for the T_h point group with no fourfold symmetry axis.[23] This wave function is expressed by a combination of Γ_4 and Γ_5 wave functions in the O_h point group, where the latter Γ_5 is more dominant. Owing to the small singlet-triplet energy splitting $\simeq 8$ K, it is expected that the quadrupole degrees of freedom will play a key role in the unconventional superconductivity as well as in the field-induced ordering. However, there is no reason to deny any contribution from other multipole degrees of freedom in the Pr singlet-triplet configuration.

To find a clue to understand the multipole contribution to the superconductivity, we focus on the Pr impurity effect on the $LaOs_4Sb_{12}$ superconductor. As mentioned above, $T_{\rm c}$ is increased by Pr substitution for La in $LaOs_4Sb_{12}$. In addition, multiband properties are indicated by thermal-transport measurement under a mag-

netic field in $PrOs_4Sb_{12}$[24] and by nuclear quadrupole resonance measurement in $(La_{1-x}Pr_x)Os_4Sb_{12}$.[15] Suppose that $LaOs_4Sb_{12}$ is a single-band superconductor and that the inelastic scattering by the Pr impurities contributes to the T_c increase, the most probable origin of the T_c increase is a quadrupolar scattering effect that leads to an effective pairing interaction that stabilizes the superconductivity, by analogy with the optical phonon-mediated pairing.[25] If a multiband picture is applicable, there are two possibilities: For the s_{++}-wave state with the same sign order parameters, interband nonmagnetic (quadrupolar) scattering is also favorable for the T_c increase by the inelastic impurity scattering, while interband magnetic (octupolar) scattering can increase T_c for the $s_{\pm}$-wave state. The relevance of the multiband scenario is closely connected to the characteristic structure of skutterudites. In $PrOs_4Sb_{12}$, each Pr ion is located at the center of the Sb_{12} icosahedron cage. The most important point is the local hybridization of the Pr $4f$-electron states with conduction bands via the Sb_{12} molecular orbitals denoted by the a_u and t_u point-group symmetries.[26,27] If the a_u-t_u orbital exchange is the most relevant for the Pr impurity scattering, the multipolar coupling in the Pr singlet-triplet configuration contributes to the T_c increase. In our previous work, we proposed a possibility of T_c increase by magnetic impurity scattering in the s_{++}-wave state erroneously instead of the $s_{\pm}$-wave state.[7,28] We will give a correct description of the impurity scattering effect on the two-band superconductivity in this case.

In this paper, we discuss the multiorbital scattering effect on the multiband superconductivity that reflects the local orbital symmetry. In the Pr singlet-triplet configuration, electrons are coupled to the quadrupoles expressed as yz, zx, and xy or the octupoles expressed as $x(y^2-z^2)$, $y(z^2-x^2)$, and $z(x^2-y^2)$ by analogy with the dipoles expressed as x, y, and z, respectively.[29] We focus on the magnetic octupolar scattering effect throughout the paper. There is a marked distinction between such multipoles and the spin when a magnetic field is introduced. For the orbital exchange scattering by a multipole moment, we find that its polarization changes as the field direction is rotated, while the spin exchange scattering is isotropic. If such orbital exchange scattering is an origin of T_c increase, an effective pairing interaction is modified by the scattering anisotropy under the field. It is expected that the anisotropy effect will be observed as the field orientation dependence of an upper critical field $H_{c2}(T)$ line. This would be conclusive evidence indicating that the orbital degrees of freedom definitely play a crucial role in the T_c increase, which is closely connected to the unique Pr atomic structure in $(La_{1-x}Pr_x)Os_4Sb_{12}$.

The paper is organized as follows. In §2, we show a typical form of the inelastic magnetic scattering that couples the O_h Γ_1 singlet and Γ_5 triplet states. In §3, we explain a gap equation for T_c increased or reduced by interband magnetic scattering as an impurity effect on the two-band s-wave superconductivity. The same formulation is applied straightforwardly to an interband nonmagnetic scattering case. The gap equation is modified by including a magnetic field effect on impurities. In §4, this argument is extended to a case of single a_u and threefold degenerate t_u bands that reflects the cubic symmetry. Owing to the Zeeman splitting of the excited triplet, T_c depends on the field direction. Since the T_c deviation is very small when the cubic symmetry is conserved, we consider a uniaxial anisotropy effect in the gap equation to elucidate the close correlation between the field-orientation-dependent T_c and the anisotropy of multipolar scattering. Finally, conclusions are given in §5.

2. Inelastic Scattering by Impurities

First, we show a typical case of the inelastic electron scattering by magnetic impurities, keeping in mind the Pr^{3+} states in $PrOs_4Sb_{12}$. We consider that the low-lying states consist of the Γ_1 singlet ground and Γ_5 triplet excited states in an O_h crystal field. They are expressed by[29]

$$|\Gamma_1\rangle = \frac{\sqrt{30}}{12}(|4\rangle + |-4\rangle) + \frac{\sqrt{21}}{6}|0\rangle, \tag{1}$$

$$\begin{cases} |\Gamma_5+\rangle = \sqrt{\dfrac{7}{8}}|3\rangle - \sqrt{\dfrac{1}{8}}|-1\rangle, \\ |\Gamma_5 0\rangle = \sqrt{\dfrac{1}{2}}(|2\rangle - |-2\rangle), \\ |\Gamma_5-\rangle = -\sqrt{\dfrac{7}{8}}|-3\rangle + \sqrt{\dfrac{1}{8}}|1\rangle, \end{cases} \tag{2}$$

where $|M\rangle$ $(M = 4, 3, \cdots, -4)$ is an eigenstate of J_z for the $J = 4$ total angular momentum. The interchange of the singlet and triplet states is caused by the local orbital exchange of electrons via the hybridization of f-orbitals with conduction bands. Since each Pr ion is located at the center of the Sb_{12} cage, the Sb_{12} molecular orbitals mediate the hybridization, which is the most pronounced feature of skutterudites. The a_u (Γ_2) molecular orbital mostly contributes to the main conduction band (a_u band), hybridizing with the f-orbitals most strongly.[26] The spin and orbitally coupled states of f-electrons are categorized as the Γ_7 representation. We also consider here that the t_u (Γ_4) orbitals participate in the secondary conduction band (t_u band), having a weaker hybridization with the Γ_8 f-electron states (see Appendix A).

Both quadrupole and octupole moments with the Γ_5 symmetry are involved in the interchange of the Pr Γ_1 and Γ_5 states. We focus on the inelastic octupolar scattering since it is unconventional that T_c can be increased by magnetic correlations. In the present case, the octupolar exchange scattering is accompanied by the a_u-t_u orbital exchange of local electrons, which is shown in Fig. 1. This effective exchange interaction is expressed by the following Hamiltonian $\mathcal{H}_{ex} = \mathcal{H}_I + \mathcal{H}'$:

$$\mathcal{H}_I = \sum_{\boldsymbol{R}_\gamma} \sum_n \delta_n a^\dagger_{\gamma n} a_{\gamma n}, \tag{3}$$

$$\mathcal{H}' = J_S \sum_{\boldsymbol{R}_\gamma} \sum_{nn'} \int \mathrm{d}\boldsymbol{r} a^\dagger_{\gamma n} a_{\gamma n'} \delta(\boldsymbol{r} - \boldsymbol{R}_\gamma) \times \boldsymbol{\psi}^\dagger(\boldsymbol{r}) \left(\hat{I}_S\right)_{nn'} \boldsymbol{\psi}(\boldsymbol{r}). \tag{4}$$

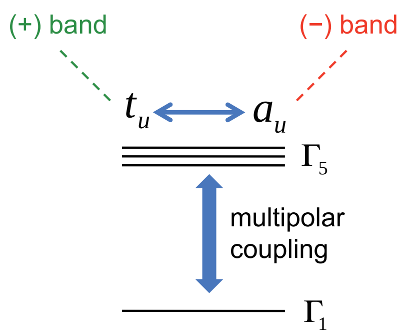

Fig. 1. Sketch of the inelastic multipolar exchange scattering with the a_u-t_u orbital exchange in the Pr singlet-triplet configuration. Here, the local t_u and a_u electrons participate in the different bands denoted by (+) and (−), respectively.

The first term $\mathcal{H}_{\rm I}$ is for the impurity states, where $\boldsymbol{R}_\gamma$ represents the position of the γth impurity and $a^\dagger_{\gamma n}$ ($a_{\gamma n}$) is the pseudo-fermion creation (annihilation) operator for the nth impurity energy level δ_n at the γth impurity site ($n = 1, 2, 3$, and 4 denote Γ_1, Γ_5+, $\Gamma_5 0$, and Γ_5-, respectively).[30] In the second term $\mathcal{H}'$, $\hat{I}_S$ represents the Γ_5-type octupolar exchange scattering of conduction electrons with the coupling constant J_S (S denotes the magnetic scattering here) that is accompanied by the interchange among the nth and n'th energy levels:

$$\left(\hat{I}_S\right)_{nn'} = (T_z)_{nn'}\,\hat{t}_z + \frac{1}{2}\,(T_+)_{nn'}\,\hat{t}_- + \frac{1}{2}\,(T_-)_{nn'}\,\hat{t}_+, \tag{5}$$

where T_η and $\hat{t}_\eta$ ($\eta = z, \pm$) are octupole operators for the impurity states and conduction electrons, respectively. Their complete expressions are given in §3 of ref. 31. We use the two-band expression $\boldsymbol{\psi}^\dagger \hat{t}_\eta \boldsymbol{\psi}$ for the octupolar exchange scattering with the a_u-t_u orbital exchange as described in Appendix A, where we have corrected the previous results.[7]

3. Gap Equation for Two-Band Superconductivity

Before discussing the multipolar scattering effect on $T_{\rm c}$, we briefly review our previous study and give a correct description for the the Pr-like impurities with the singlet-triplet configuration, focusing on how to derive a gap equation for the two-band s_{++}-wave and $s_\pm$-wave superconducting states.[7] A magnetic field effect, which modifies an effective pairing interaction, is also taken into account in the gap equation. In Table I, we summarize the effective interaction type, which is either attractive or repulsive, mediated by the interband magnetic (octupolar) scattering or nonmagnetic (quadrupolar) scattering impurities in each s-wave state.

3.1 Formulation

To describe the superconductivity, we start from the following Hamiltonian for the two-band ($\mu = \pm$) electrons:

Table I. Effective pairing interaction type mediated by the interband magnetic or nonmagnetic (octupolar or quadrupolar, respectively, in the O_h Γ_1-Γ_5 configuration) scattering impurities: A (attractive) or R (repulsive). It depends on the pairing type used.

Scattering type	Pairing type	Interaction type
magnetic	s_{++}-wave	R
	$s_\pm$-wave	A
nonmagnetic	s_{++}-wave	A
	$s_\pm$-wave	R

$$\mathcal{H}_{\rm C} = \sum_{\mu\sigma}\int {\rm d}\boldsymbol{r}\,\psi^\dagger_{\mu\sigma}(\boldsymbol{r})\epsilon(-{\rm i}\nabla)\psi_{\mu\sigma}(\boldsymbol{r}) - \sum_{\mu}\Delta_\mu\int {\rm d}\boldsymbol{r}\left[\psi^\dagger_{\mu\uparrow}(\boldsymbol{r})\psi^\dagger_{\mu\downarrow}(\boldsymbol{r}) + \psi_{\mu\downarrow}(\boldsymbol{r})\psi_{\mu\uparrow}(\boldsymbol{r})\right]. \tag{6}$$

Here, we assume that both bands are identical and the order parameters have the same amplitude $|\Delta_+| = |\Delta_-| = \Delta$ for simplicity. The operator $\epsilon(-{\rm i}\nabla) = -\nabla^2/(2m_{\rm e}) - E_{\rm F}$ expresses the kinetic energy measured from the Fermi energy $E_{\rm F}$, where $m_{\rm e}$ is the electron mass and $\hbar = 1$. It is convenient to introduce the 8×8 matrix form of the thermal Green's function

$$\hat{G}(\tau, \boldsymbol{r}, \boldsymbol{r}') = -\langle T\boldsymbol{\Psi}(\boldsymbol{r}, \tau)\boldsymbol{\Psi}^\dagger(\boldsymbol{r}', 0)\rangle, \tag{7}$$

with the eight-dimensional vectors $\boldsymbol{\Psi}(\boldsymbol{r})$ and $\boldsymbol{\Psi}^\dagger(\boldsymbol{r})$ for the two-band electrons defined as

$$\boldsymbol{\Psi} = \begin{pmatrix} \boldsymbol{\Psi}_+ \\ \boldsymbol{\Psi}_- \end{pmatrix}, \quad \boldsymbol{\Psi}^\dagger = \begin{pmatrix} \boldsymbol{\Psi}^\dagger_+ & \boldsymbol{\Psi}^\dagger_- \end{pmatrix}, \tag{8}$$

and

$$\boldsymbol{\Psi}_\mu(\boldsymbol{r}) = \begin{pmatrix} \psi_{\mu\uparrow}(\boldsymbol{r}) \\ \psi_{\mu\downarrow}(\boldsymbol{r}) \\ \psi^\dagger_{\mu\uparrow}(\boldsymbol{r}) \\ \psi^\dagger_{\mu\downarrow}(\boldsymbol{r}) \end{pmatrix},$$

$$\boldsymbol{\Psi}^\dagger_\mu(\boldsymbol{r}) = \begin{pmatrix} \psi^\dagger_{\mu\uparrow}(\boldsymbol{r}) & \psi^\dagger_{\mu\downarrow}(\boldsymbol{r}) & \psi_{\mu\uparrow}(\boldsymbol{r}) & \psi_{\mu\downarrow}(\boldsymbol{r}) \end{pmatrix}. \tag{9}$$

Their Heisenberg representations are written as

$$\boldsymbol{\Psi}_\mu(\boldsymbol{r}, \tau) = {\rm e}^{\mathcal{H}\tau}\boldsymbol{\Psi}_\mu(\boldsymbol{r}){\rm e}^{-\mathcal{H}\tau}, \quad \boldsymbol{\Psi}^\dagger_\mu(\boldsymbol{r}, \tau) = {\rm e}^{\mathcal{H}\tau}\boldsymbol{\Psi}^\dagger_\mu(\boldsymbol{r}){\rm e}^{-\mathcal{H}\tau}. \tag{10}$$

In the absence of impurity scattering, the unperturbed Green's function is Fourier-transformed to

$$\hat{G}_0({\rm i}\omega_l, \boldsymbol{k}) = -\frac{{\rm i}\omega_l + \epsilon_{\boldsymbol{k}}\hat{\rho}_3 + \hat{\Delta}\hat{\rho}_2\hat{\sigma}_2}{\omega_l^2 + \epsilon_{\boldsymbol{k}}^2 + \Delta^2}, \tag{11}$$

where $\hat{\sigma}_\alpha$ is the Pauli matrix for the spin space and $\hat{\rho}_\alpha$ is that for the particle-hole space ($\alpha = 1, 2$, and 3 correspond to x, y, and z, respectively), and $\epsilon_{\boldsymbol{k}} = \boldsymbol{k}^2/(2m_{\rm e}) - E_{\rm F}$. The two-band superconductivity is expressed with another Pauli matrix $\hat{\tau}_\alpha$ in the band space as

$$\hat{\Delta} = \frac{\Delta_+}{2}(1 + \hat{\tau}_3) + \frac{\Delta_-}{2}(1 - \hat{\tau}_3). \tag{12}$$

We consider the magnetic (octupolar) scattering effect

on T_c when the impurities are distributed randomly in the two-band s-wave superconductor, which is expressed on the right-hand side of the following linearized gap equation:[7,8]

$$\frac{8T_\mathrm{c}}{\pi}\tau^S \log\frac{T_\mathrm{c}}{T_\mathrm{c0}}\begin{pmatrix}\Delta_+\\ \Delta_-\end{pmatrix} = \begin{pmatrix} f_\omega & f_\Delta \\ f_\Delta & f_\omega\end{pmatrix}\begin{pmatrix}\Delta_+\\ \Delta_-\end{pmatrix}, \tag{13}$$

where T_c (T_c0) is the transition temperature in the presence (absence) of impurities. f_Δ and f_ω represent self-energies corresponding to the order parameter and Matsubara frequency components, respectively. On the basis of the unperturbed Hamiltonian $\mathcal{H}_\mathrm{C}+\mathcal{H}_\mathrm{I}$ in eqs. (6) and (3), the self-energy is obtained as

$$\begin{aligned}\hat{\Sigma}_S(\mathrm{i}\omega_l) = &- n_\mathrm{imp}T^2\sum_{n\neq n'}\sum_{\omega_1\omega_2}\frac{1}{\mathrm{i}\omega_1-\delta_n}\frac{1}{\mathrm{i}\omega_2-\delta_{n'}}\\ &\times J_S^2\frac{1}{\Omega}\sum_{\boldsymbol{k}}\left(\hat{I}_S\right)_{nn'}\hat{G}_0(\mathrm{i}\omega_l+\mathrm{i}\omega_1-\mathrm{i}\omega_2,\boldsymbol{k})\\ &\times\left(\hat{I}_S\right)_{n'n}\end{aligned} \tag{14}$$

in the second Born approximation by $\mathcal{H}'$ in eq. (4) for the Γ_5 magnetic type of effective exchange scattering $\hat{I}_S$ in eq. (5). Here, n_imp is the impurity density, T is the temperature ($k_\mathrm{B}=1$), and Ω represents the system volume. By analogy with the optical phonon case, the inelastic impurity scattering leads to an effective pairing interaction. After calculating the self-energy terms,

$$\Sigma_\Delta(\mathrm{i}\omega_l) = \frac{1}{8}\mathrm{Tr}\left[\hat{\rho}_2\hat{\sigma}_2\hat{\Sigma}_S(\mathrm{i}\omega_l)\right],\quad \Sigma_\omega(\mathrm{i}\omega_l)=\frac{1}{8}\mathrm{Tr}\hat{\Sigma}_S(\mathrm{i}\omega_l), \tag{15}$$

where 1/8 is the normalization factor in the $\hat{\tau}\otimes\hat{\rho}\otimes\hat{\sigma}$ space ($\hat{\tau}$ for the band space, $\hat{\rho}$ for the particle-hole space and $\hat{\sigma}$ for the spin space), we obtain

$$\begin{aligned}\pi T_\mathrm{c}\sum_l\frac{1}{|\omega_l|}\Sigma_\Delta(\mathrm{i}\omega_l) &= -\frac{\pi}{8T_\mathrm{c}\tau^S}f_\Delta(x)>0,\\ \pi T_\mathrm{c}\sum_l\frac{\mathrm{i}}{|\omega_l|}\frac{\Sigma_\omega(\mathrm{i}\omega_l)}{\omega_l} &= -\frac{\pi}{8T_\mathrm{c}\tau^S}f_\omega(x)>0,\end{aligned} \tag{16}$$

where x represents the energy difference between the Γ_1 singlet ground and Γ_5 triplet excited states as

$$x=\frac{\delta_{\Gamma_5}-\delta_{\Gamma_1}}{2T_\mathrm{c}}. \tag{17}$$

We define the lifetime due to the magnetic impurity scattering as

$$\frac{1}{\tau^S}=2\pi n_\mathrm{imp}N_0\left(\frac{J_S}{2}\right)^2, \tag{18}$$

where N_0 represents the density of electronic states at the Fermi energy. In the absence of a magnetic field, both $f_\Delta(x)$ and $f_\omega(x)$ are independent of θ and ϕ related to the local hybridization defined in eq. (A·10). In eq. (13), the matrix gives the higher eigenvalue $f(x)=-f_\Delta(x)+f_\omega(x)>0$ for the higher T_c in the $s_\pm$-wave state ($\Delta_+/\Delta_-=-1$). The explicit representation of $f(x)$ is given in Appendix B. The s_{++}-wave state ($\Delta_+/\Delta_-=1$) is for the lower T_c. In the same manner, for the nonmagnetic (quadrupolar) scattering in Appendix A, the gap equation is given by

$$\frac{8T_\mathrm{c}}{\pi}\tau^Q \log\frac{T_\mathrm{c}}{T_\mathrm{c0}}\begin{pmatrix}\Delta_+\\ \Delta_-\end{pmatrix} = \begin{pmatrix} f_\omega & -f_\Delta \\ -f_\Delta & f_\omega\end{pmatrix}\begin{pmatrix}\Delta_+\\ \Delta_-\end{pmatrix}, \tag{19}$$

where τ^Q is the corresponding lifetime, which leads to the T_c increase in the s_{++}-wave state (see Table I).

3.2 *Magnetic field effect*

Next, we consider a magnetic field effect that is weak enough not to directly affect the superconducting order parameter and put aside the field coupling with conduction electrons. In the present case, the Zeeman splitting of the impurity triplet states reduces the effective pairing interaction and the a_u-t_u scattering depends on the field direction. Consequently, the reduced T_c exhibits the field orientation dependence.

It is convenient to choose the quantization axis in the direction of the applied magnetic field $\boldsymbol{H}$. The Zeeman splitting is expressed as

$$\langle\pm|-\boldsymbol{J}\cdot\boldsymbol{h}|\pm\rangle=\mp h_\mathrm{t},\quad \langle 0|-\boldsymbol{J}\cdot\boldsymbol{h}|0\rangle=0, \tag{20}$$

where $h_\mathrm{t}=(5/2)h$ and $h=|\boldsymbol{h}|$ ($\boldsymbol{h}=g_J\mu_\mathrm{B}\boldsymbol{H}$: g_J is the Landé g factor) for the Γ_5 triplet, and $|n\rangle$ ($n=+,0,-$) is an eigenstate of $-\boldsymbol{J}\cdot\boldsymbol{h}$ expressed by a combination of the three Γ_5 states in eq. (2). For the interchange between the singlet and triplet states, the T_η operators in eq. (5) correspondingly depend on the field directions $(\bar{h}_x,\bar{h}_y,\bar{h}_z)$, as indicated in eqs. (A·11) and (A·12). The magnetic field effect only modifies $f_{\xi=\omega,\Delta}$ in the gap equation [eq. (13)] as

$$f_\xi\to C_hf_\xi(x_0)+\frac{1}{2}(1-C_h)[f_\xi(x_+)+f_\xi(x_-)], \tag{21}$$

where the energy difference x_n ($n=+,0,-$ for the excited triplet) and the anisotropy coefficient C_h are defined as

$$x_n=\frac{\delta_n-\delta_{\Gamma_1}}{2T_\mathrm{c}}, \tag{22}$$

$$C_h=\mathrm{Tr}_{\hat{\tau}\hat{\sigma}}\left[\langle\Gamma_1|\hat{I}_S|0\rangle\langle 0|\hat{I}_S|\Gamma_1\rangle\right], \tag{23}$$

respectively. Here, $\mathrm{Tr}_{\hat{\tau}\hat{\sigma}}$ indicates the trace of $[\cdots]$ in calculating with the 4×4 matrices in eqs. (A·7) and (A·8).

4. Application

In this section, we consider a case of the single a_u and threefold degenerate t_u bands as an extension of the above two-band case (see Fig. 2). The inclusion of the threefold degeneracy is required in the minimum model for the conservation of the cubic symmetry. We assume that these bands are combined with each other only through the impurity interband scattering effect. Since it is shown that T_c is not markedly field-orientation-dependent under the cubic symmetry, we introduce a uniaxial anisotropy effect phenomenologically to check how T_c is affected by the orbital (multipole) anisotropy of impurity scattering. Finally, we give a comment on $H_{\mathrm{c2}}(T)$ in the vicinity of T_c that reflects the anisotropic

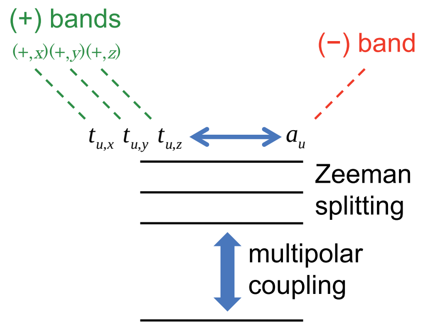

Fig. 2. Sketch of the inelastic multipolar exchange scattering in the a_u and threefold degenerate t_u band case. Each local $t_{u,\alpha}$ electron participates in the corresponding $(+,\alpha)$ band ($\alpha = x, y, z$), while the local a_u electron is transferred to the single $(-)$ band.

scattering.

4.1 a_u and threefold degenerate t_u band case

When a magnetic field is applied, it is generally observable that under the cubic symmetry, T_c decreases as

$$T_c(h=0) - T_c = a_2 h_t^2 + a_4 h_t^4, \qquad (24)$$

where $h_t = (5/2)h$ is the Zeeman splitting, a_2 is a positive constant, and a_4 is the field-orientation-dependent parameter

$$a_4 \propto \text{const.} + (\bar{h}_x^4 + \bar{h}_y^4 + \bar{h}_z^4). \qquad (25)$$

Here, we simplify the mixing of the local t_u (x, y, z) orbitals and the $+$ band. Instead, for the conservation of the cubic symmetry, we introduce the threefold degenerate t_u-dominant bands denoted by $(+,\alpha)$, where $\alpha = x, y, z$, which hybridize with the f-orbitals most strongly in the directions of three principal axes. The corresponding a_u-t_u scattering anisotropy in eq. (A·15) is given by

$$C_{h,x} \equiv C_h(\theta = \frac{\pi}{2}, \phi = 0) = \frac{1}{6} + \frac{1}{2}\bar{h}_x^2,$$
$$C_{h,y} \equiv C_h(\theta = \frac{\pi}{2}, \phi = \frac{\pi}{2}) = \frac{1}{6} + \frac{1}{2}\bar{h}_y^2,$$
$$C_{h,z} \equiv C_h(\theta = 0) = \frac{1}{6} + \frac{1}{2}\bar{h}_z^2. \qquad (26)$$

When the single a_u and threefold degenerate t_u bands are taken into account, the gap equation [eq. (13)] is extended to the following eigenvalue problem:

$$\frac{T_c}{T_{c0}} \log \frac{T_c}{T_{c0}} \begin{pmatrix} \Delta_{+,x} \\ \Delta_{+,y} \\ \Delta_{+,z} \\ \Delta_- \end{pmatrix} = \hat{\Lambda} \begin{pmatrix} \Delta_{+,x} \\ \Delta_{+,y} \\ \Delta_{+,z} \\ \Delta_- \end{pmatrix},$$

$$\hat{\Lambda} = \alpha_S \begin{pmatrix} F_{\omega,x} & 0 & 0 & F_{\Delta,x} \\ 0 & F_{\omega,y} & 0 & F_{\Delta,y} \\ 0 & 0 & F_{\omega,z} & F_{\Delta,z} \\ F_{\Delta,x} & F_{\Delta,y} & F_{\Delta,z} & \sum_\alpha F_{\omega,\alpha} \end{pmatrix}. \qquad (27)$$

Here, $\Delta_{+,\alpha}$ $(\alpha = x, y, z)$ is the order parameter for the $(+,\alpha)$ band and no interband pairing is taken into account. The magnetic scattering strength α_S is given by

$$\alpha_S = \frac{\pi}{8T_{c0}\tau^S} \propto \frac{n_{\rm imp} N_0 J_S^2}{T_{c0}}. \qquad (28)$$

In the presence of a magnetic field, the matrix elements of $\hat{\Lambda}$ for ξ $(= \omega, \Delta)$ are given in the same manner as eq. (21):

$$F_{\xi,\alpha} = C_{h,\alpha} f_\xi(x_0) + \frac{1}{2}(1 - C_{h,\alpha})[f_\xi(x_+) + f_\xi(x_-)]. \qquad (29)$$

The excited triplet energy levels are split as

$$x_0 = \frac{\delta_0 - \delta_{\Gamma_1}}{2T_c}, \quad x_\pm = x_0 \mp x_h \quad \left(x_h \equiv \frac{h_t}{2T_c}\right), \qquad (30)$$

owing to the Zeeman splitting $h_t = (5/2)h$ of the Γ_5 triplet. When the field direction is so rotated as to pass through the [111] axis, both x and y components are taken to be equivalent $(\bar{h}_x = \bar{h}_y)$. In Appendix C, we show that the field-direction $(\bar{h}_z)$-dependent term is extracted from $F_{\xi,\alpha}$.

The highest eigenvalue of $\hat{\Lambda}$ determines T_c. When a magnetic field is absent $(x_h = 0)$, $F_{\xi,\alpha} = f_{\xi,\alpha} = f_\xi$ in eq. (B·1) leads to

$$\frac{T_c}{T_{c0}} \log \frac{T_c}{T_{c0}} = \alpha_S \left(2f_\omega + \sqrt{f_\omega^2 + 3f_\Delta^2}\right). \qquad (31)$$

The x_0 dependence of this equation is similar to $f(x)$ in Fig. B·1 that corresponds to the two-band case. The calculated T_c is plotted for various values of the singlet-triplet level splitting $(\delta_{\Gamma_5} - \delta_{\Gamma_1})/T_{c0}$ in Fig. 3. The α_S dependence is not sensibly affected by the large change in crystal field level for $(\delta_{\Gamma_5} - \delta_{\Gamma_1}) \gtrsim 10T_{c0}$. The monotonic increase in T_c with $\alpha_S \propto n_{\rm imp}$ explains well the Pr concentration x dependence of T_c measured in $(La_{1-x}Pr_x)Os_4Sb_{12}$ at the relatively small x values where the Pr ions are regarded as impurities.[15]

In the presence of a magnetic field, the effect of η_ξ in eq. (C·2) appears at the field-orientation-dependent T_c in eq. (24) such that

$$a_4 \sim \frac{1}{2} - \bar{h}_z^2 + \frac{3}{2}\bar{h}_z^4, \qquad (32)$$

where $\bar{h}_x = \bar{h}_y$ is retained. This leads to

$$\frac{a_{4[001]} - a_{4[111]}}{a_{4[110]} - a_{4[111]}} = 4. \qquad (33)$$

In the present model, we find that the difference $(T_{c[001]} - T_{c[111]})$ is of the order of h^4, less than $10^{-4}T_c$ even for a larger magnetic field $x_h > 1$ since $|a_4|$ is extremely smaller than a_2. Therefore, η_ξ is negligible and T_c can be regarded as isotropic, which is determined by

$$\frac{T_c}{T_{c0}} \log \frac{T_c}{T_{c0}} = \alpha_S \left(2F_\omega + \sqrt{F_\omega^2 + 3F_\Delta^2}\right) \qquad (34)$$

with the same form as eq. (31). The decrease in T_c with increasing h comes from

$$F(x_0, x_h) - f(x_0) = \frac{1}{3} f''(x_0) x_h^2 < 0, \qquad (35)$$

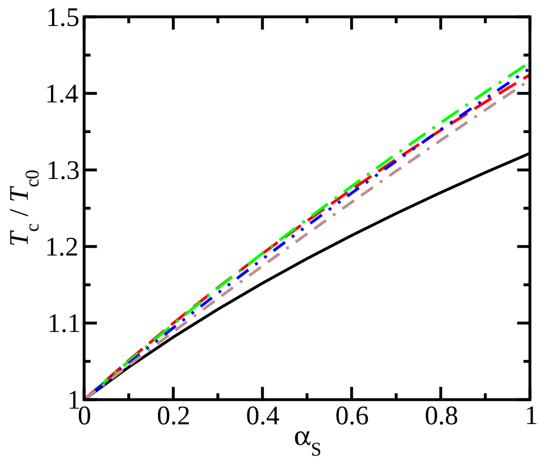

Fig. 3. T_c/T_{c0} of the $s_{\pm}$-wave state as a function of the interband magnetic scattering strength α_S for various values of the level splitting $(\delta_{\Gamma_5} - \delta_{\Gamma_1})/T_{c0} = 5$ (solid line), 10 (dashed line), 15 (one-dashed and one-dotted line), 20 (one-dashed and two-dotted line), and 25 (two-dashed and one-dotted line). The same dependence is obtained for the interband nonmagnetic scattering in the s_{++}-wave state.

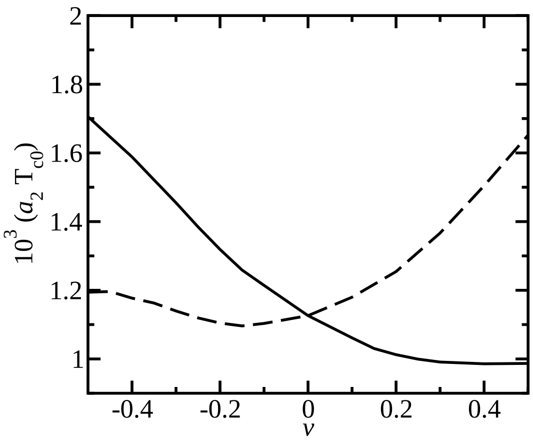

Fig. 4. Anisotropy v dependence of $a_2(\theta_h)$ for $\alpha_S = 1$ and $(\delta_0 - \delta_{\Gamma_1})/T_{c0} = 10$. The solid and dashed lines are the plots for $\boldsymbol{h}\|[001]$ $(\theta_h = 0)$ and $\boldsymbol{h}\|[110]$ $(\theta_h = \pi/2)$, respectively. a_2 exhibits the $\cos 2\theta_h$ oscillation between $a_2(0)$ and $a_2(\pi/2)$.

where $F = -F_\Delta + F_\omega$ and $f = -f_\Delta + f_\omega > 0$, calculated using eq. (C·1). It should be noted that T_c could be increased by applying a magnetic field if $f(x)$ had some features to satisfy $f''(x_0) > 0$.

4.2 *Uniaxial anisotropy effect*

As discussed above, no distinct feature is found in the field orientation dependence of T_c in the rotation of the field direction. This is due to the equivalency of x, y, and z components in the orbital symmetry and the constant a_2 in eq. (24). Here, we check how the T_c deviation is increased by lowering the crystal field symmetry from O_h. To show this explicitly, we introduce a uniaxially anisotropic deviation from O_h. Consequently, a_2 has a linear dependence on $\bar{h}_z^2$, which leads to the field angle dependence as $\cos 2\theta_h$ $(\cos\theta_h = \bar{h}_z)$, reflecting the twofold symmetry.

Here, we represent the uniaxial anisotropy by the single phenomenological parameter v in the gap equation [eq. (27)], modifying $F_{\xi,\alpha}$ as

$$F_{\xi,\alpha} \to (1-v)F_{\xi,\alpha} \quad (\alpha = x, y), \quad F_{\xi,z} \to (1+2v)F_{\xi,z}. \tag{36}$$

For the impurity states, only the Zeeman splitting x_h is considered. We assume that the main contribution to v comes from the change in local orbital hybridization amplitude owing to the lowering of the symmetry. If the limits $v \to 1$ and $\alpha_S \to \alpha_S/3$ are considered, eq. (27) is reduced to the two-band case in eq. (13). Around the z-axis, we find that a_2 in eq. (24) is independent of $(\bar{h}_x, \bar{h}_y)$ since the fourfold symmetry is conserved. In the following argument, we calculate

$$a_2(\theta_h) = \frac{1}{2}\left(a_{2[001]} + a_{2[110]}\right) + \frac{1}{2}\left(a_{2[001]} - a_{2[110]}\right)\cos 2\theta_h \tag{37}$$

for various v values, keeping $\bar{h}_x = \bar{h}_y$ in eq. (27). As it is expected, the T_c deviation becomes more distinct as the crystal field anisotropy v increases. Figure 4 shows how a_2 increases with $|v|$ for both $\boldsymbol{h}\|[001]$ $(\theta_h = 0)$ and $\boldsymbol{h}\|[110]$ $(\theta_h = \pi/2)$. The maximum of T_c (minimum of a_2) is given by $T_{c[001]}$ when $v > 0$ and by $T_{c[110]}$ when $v < 0$. It is necessary for the larger amplitude of oscillation in eq. (37) to introduce a stronger anisotropy. For $v = 0.5$, the difference $(a_{2[110]} - a_{2[001]})$ is estimated as $\sim 10^{-3}/T_c$ in Fig. 4. This indicates that the amplitude of T_c oscillation $(\propto h^2)$ is about 0.1% of T_c at $h_t/T_c \simeq 1$ and 1% at $h_t/T_c \simeq 3$ (h_t represents the Zeeman splitting of the excited triplet). If the crystal field anisotropy is much smaller, it is more difficult to obtain the field angle θ_h dependence of T_c. We note that η_ξ in eq. (C·2) is responsible for the θ_h dependence, so that T_c at $\bar{h}_z = 1/\sqrt{3}$ for $v \neq 0$ ($T_{c[111]}$ in the cubic symmetry for $v = 0$) directly reflects the crystal field anisotropy (t_u-orbital anisotropy) since η_ξ vanishes at $\bar{h}_z = 1/\sqrt{3}$. Therefore, the anisotropy of multipolar scattering itself appears in the T_c deviation from $T_c(\bar{h}_z = 1/\sqrt{3})$.

In a real system, this anisotropy effect can be observed as the field orientation dependence of the upper critical field h_{c2} near T_c at $h = 0$. We can estimate h_{c2} in the framework of the conventional Ginzburg-Landau (GL) theory, taking into account a diamagnetic effect in the GL expansion of a free energy.[32)] h_{c2} is given by Δt $(= 1 - T/T_c)$ expansion as[33)]

$$h_{c2} = c_1\Delta t + c_2(\Delta t)^2 + \cdots, \tag{38}$$

with $c_1 > 0$. In the present case, the effective pairing interaction depends on the crystal field energy levels coupled to the magnetic field, and T_c is reduced as

$$T_c = T_c(0) - a_2(\theta_h)h_{c2}^2 \quad [T_c(0) \equiv T_c(h=0)]. \tag{39}$$

Substituting it for T_c in eq. (38), we obtain

$$h_{c2} \simeq c_1\left[1 - \frac{T}{T_c(0)}\right] + \left[c_2 - \frac{c_1^3}{T_c(0)}a_2(\theta_h)\right]\left[1 - \frac{T}{T_c(0)}\right]^2. \tag{40}$$

When the cubic symmetry is conserved, h_{c2} is invariant against the rotation of the field direction since $a_2(\theta_h)$ is

a constant for $v = 0$. If a uniaxial anisotropy is applied, for instance, by pressure measurement, the field-angle-dependent $h_{c2}(T)$ lines could be observed in the superconducting phase. This is more promising for a large c_1 that is related to the GL parameter. This provides us with conclusive evidence of the multiband picture proposed in our theory. The multipole moments in the f-electron states play an important role in the anisotropic $h_{c2}(T)$, which is analogous to the quadrupole ordering transition temperature $T_{\rm Q}(H)$ with the field orientation dependence, as observed in $PrPb_3$[34,35] or as predicted for CeB_6 in a high magnetic field.[36]

5. Conclusion

We have studied a magnetic field effect on $T_{\rm c}$ increased by inelastic scattering for the singlet-triplet configuration in impurities. The $T_{\rm c}$ increase can be expected for either the interband magnetic scattering in the $s_\pm$-wave state or the nonmagnetic scattering in the s_{++}-wave state. We have focused on the Γ_5-type octupolar exchange scattering in the former. The same argument is applicable to the Γ_5-type quadrupolar exchange scattering in the latter. Owing to the anisotropy of multipolar scattering [η_ξ in eq. (C·2)], $T_{\rm c}$ exhibits the field orientation dependence. Since the $T_{\rm c}$ deviation ($\propto h^4$) is very small in the cubic symmetric environment, we have introduced a uniaxial anisotropy into the degenerate t_u orbitals to clarify the multipolar scattering effect on $T_{\rm c}$. The multipolar scattering anisotropy itself appears in the twofold symmetric oscillation of $T_{\rm c}$ with the rotation of the field direction, and the amplitude of oscillation increases proportionally to h^2. This can be confirmed by observing the splitting of an $H_{c2}(T)$ line near $T_{\rm c}$ with a change in field angle, although a uniaxial anisotropic field is required to produce a clear difference between the two field directions, as discussed in §4.2.

Thus, we have clarified the roles of multipole degrees of freedom in multiband superconductors. The key is that the local orbital exchange scattering is directly connected to the interband scattering via the hybridization of f-orbitals with each band. The local orbital anisotropy in eq. (C·2) appears clearly at the field-orientation-dependent $T_{\rm c}$, which is related to the field orientation dependence in eq. (A·15) for the octupolar scattering. This is not expected for the spin exchange scattering in a single band. If each $\hat{t}_\eta$ ($\eta = z, \pm$) is replaced by the Pauli matrix $\hat{\sigma}_\eta$ ($\hat{\sigma}_\pm = \hat{\sigma}_x \pm {\rm i}\hat{\sigma}_y$) in eq. (A·14), the calculated C_h becomes a constant, indicating that the spin exchange scattering is invariant against the rotation of the field direction. Therefore, the field-orientation-dependent $T_{\rm c}$, i.e., the anisotropic H_{c2}, would be positive evidence for the multiband picture proposed here.

In a real system, the quadrupolar scattering coexists with the octupolar scattering for the O_h Γ_1 singlet and Γ_5 triplet configurations.[7] The quadrupolar scattering strength α_Q is defined as α_S. Unlike the magnetic case, the interband nonmagnetic scattering suppresses $T_{\rm c}$ in the $s_\pm$-wave state, which is due to the sign reversal of $F_{\Delta,\alpha}$ ($\alpha = x, y, z$) in the gap equation [eq. (27)]. The competition of magnetic and nonmagnetic scattering effects can be taken into account by modifying

$$\alpha_S F_{\omega,\alpha} \to (\alpha_S + \alpha_Q) F_{\omega,\alpha}, \quad \alpha_S F_{\Delta,\alpha} \to (\alpha_S - \alpha_Q) F_{\Delta,\alpha} \tag{41}$$

in eq. (27). The calculated $T_{\rm c}$ decreases linearly with α_Q/α_S in the $s_\pm$-wave state ($\Delta_{+,\alpha}\Delta_- < 0$). For the strong spin-orbit coupling, $\alpha_Q/\alpha_S = 1/9$ is derived from the Anderson model including the effective exchange scattering of the $J = 5/2$ ($\Gamma_7 \oplus \Gamma_8$ for O_h in Appendix A) electrons due to a single impurity.[7,31] This ratio of scattering strengths leads to only an approximately 10% reduction in $T_{\rm c}$. Therefore, the $T_{\rm c}$ increase holds for the dominant magnetic scattering in the $s_\pm$-wave state. On the other hand, in the s_{++}-wave state ($\Delta_{+,\alpha}\Delta_- > 0$), the nonmagnetic scattering contributes to the $T_{\rm c}$ increase for $\alpha_Q \gg \alpha_S$.[7] Experimentally, it has not been established which scattering is more dominant, magnetic or nonmagnetic, as the Pr impurity effect on the $LaOs_4Sb_{12}$ superconductor. We would like to point out that $T_{\rm c}$ can also be suppressed by intraband magnetic scattering that corresponds to the spin exchange scattering in the single a_u band that we have neglected. Since the a_u electrons are coupled only to the excited triplet in the strong spin-orbit coupling case,[31] the intraband scattering effect on $T_{\rm c}$ is negligibly small.

As mentioned in §1, the T_h symmetry is another feature of the skutterudites, leading to the mixing of the O_h Γ_4 and Γ_5 wave functions of the triplet states as[19,20]

$$|\Gamma_4^{(2)}\rangle = \sqrt{1-d^2}|\Gamma_5\rangle + d|\Gamma_4\rangle, \tag{42}$$

where d represents the deviation from the O_h symmetry. Since d is relatively small, the T_h effect modifies η_ξ slightly in eq. (C·2). On the other hand, the magnetic field couples the ground state and one of the triplet states via the Van Vleck process, which shifts the energy difference x_n in eq. (22) by $\sim d^2h^2/(\delta_0 - \delta_{\Gamma_1})$. Thus, the T_h deviations from O_h only give minor corrections to the present results as long as the magnetic field is not large. It should be noted that the magnetic field effect on $T_{\rm c}$ is more sensitive to the local hybridization of f-electrons with conduction bands that we have assumed to be the strongest in the directions of three principal axes, leading to the maximum or minimum $T_{\rm c}$ in the field orientation dependence.

Finally, we would like to refer to a few experimental studies to elucidate the crucial roles of the localized Pr $4f$-electrons in the superconductivity. In $Pr_xOs_4Sb_{12}$ synthesized under a high pressure, the resistivity and magnetization data show the close correlation between the Pr singlet-triplet energy splitting and $T_{\rm c}$.[37] The recent nuclear magnetic resonance study indicates the relevance of magnetic multipole (dipole and octupole) fluctuations for mass enhancement in $PrOs_4Sb_{12}$.[38] For comparison with our scenario in the future, systematic experimental studies of $H_{c2}(T)$ in $(La_{1-x}Pr_x)Os_4Sb_{12}$ are highly desired, following the detailed analysis of $H_{c2}(T)$ in $PrOs_4Sb_{12}$ reported previously.[39] The observation of the anisotropic $H_{c2}(T)$ is worth testing under the uniaxial pressure that could enhance the Pr multipolar scattering anisotropy in a magnetic field.

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Appendix A: Interband Impurity Scattering with a_u-t_u Orbital Exchange

The single f-electron states with the $J = 5/2$ ($J_z = 5/2, 3/2, \cdots, -5/2$) total angular momentum are classified into the O_h symmetric states as[40]

$$\begin{cases} |\Gamma_{8,3/2}\rangle = -\sqrt{\frac{1}{6}}|3/2\rangle - \sqrt{\frac{5}{6}}|-5/2\rangle, \\ |\Gamma_{8,1/2}\rangle = |1/2\rangle, \\ |\Gamma_{8,-1/2}\rangle = -|-1/2\rangle, \\ |\Gamma_{8,-3/2}\rangle = \sqrt{\frac{1}{6}}|-3/2\rangle + \sqrt{\frac{5}{6}}|5/2\rangle, \end{cases} \tag{A·1}$$

$$\begin{cases} |\Gamma_{7,1/2}\rangle = \sqrt{\frac{5}{6}}|-3/2\rangle - \sqrt{\frac{1}{6}}|5/2\rangle, \\ |\Gamma_{7,-1/2}\rangle = \sqrt{\frac{5}{6}}|3/2\rangle - \sqrt{\frac{1}{6}}|-5/2\rangle. \end{cases} \tag{A·2}$$

The fourfold degenerate Γ_8 wave functions mix with the threefold degenerate t_u (x, y, z) orbitals as

$$\begin{aligned} |\Gamma_{8,-3/2}\rangle &\leftrightarrow \frac{1}{\sqrt{2}}(|x,\downarrow\rangle - \mathrm{i}|y,\downarrow\rangle), \\ |\Gamma_{8,3/2}\rangle &\leftrightarrow -\frac{1}{\sqrt{2}}(|x,\uparrow\rangle + \mathrm{i}|y,\uparrow\rangle), \\ |\Gamma_{8,1/2}\rangle &\leftrightarrow \frac{1}{\sqrt{3}}\left[\sqrt{2}|z,\uparrow\rangle - \frac{1}{\sqrt{2}}(|x,\downarrow\rangle + \mathrm{i}|y,\downarrow\rangle)\right], \\ |\Gamma_{8,-1/2}\rangle &\leftrightarrow \frac{1}{\sqrt{3}}\left[\sqrt{2}|z,\downarrow\rangle + \frac{1}{\sqrt{2}}(|x,\uparrow\rangle - \mathrm{i}|y,\uparrow\rangle)\right]. \end{aligned} \tag{A·3}$$

In the same manner, the doubly degenerate Γ_7 electrons are directly transferred to the single a_u (xyz) orbital as

$$\begin{aligned} |\Gamma_{7,1/2}\rangle &\leftrightarrow \mathrm{i}\ |xyz,\uparrow\rangle, \\ |\Gamma_{7,-1/2}\rangle &\leftrightarrow \mathrm{i}\ |xyz,\downarrow\rangle. \end{aligned} \tag{A·4}$$

In eq. (5), the T_η octupole operators couple both the Γ_1 and Γ_5 states, and their matrix expressions are given by[7]

$$T_z = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \tag{A·5}$$

$$T_+ = T_-^\dagger = \sqrt{2}\begin{pmatrix} 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \tag{A·6}$$

The interchange of the singlet ground and triplet excited states occurs via exchange in Γ_7 and Γ_8 local electrons hybridizing with the a_u and t_u bands, respectively. Introducing $\boldsymbol{\psi} = (\psi_{+\uparrow}\ \psi_{+\downarrow}\ \psi_{-\uparrow}\ \psi_{-\downarrow})^t$ for the electrons, where $\psi_{\mu\sigma}$ is the field operator for the $\mu = +$ (t_u) and $\mu = -$ (a_u) bands with the spin σ ($=\uparrow, \downarrow$), we present the typical octupolar exchange operators with the following matrix expressions:[7]

$$\hat{t}_z = \mathrm{i}\frac{1}{2}\begin{pmatrix} 0 & 0 & -c & -s_2 e^{-\mathrm{i}\phi} \\ 0 & 0 & s_2 e^{\mathrm{i}\phi} & -c \\ c & -s_2 e^{-\mathrm{i}\phi} & 0 & 0 \\ s_2 e^{\mathrm{i}\phi} & c & 0 & 0 \end{pmatrix}, \tag{A·7}$$

$$\hat{t}_+ = \hat{t}_-^\dagger = \mathrm{i}\frac{1}{2}\begin{pmatrix} 0 & 0 & -\sqrt{3}s_1 e^{\mathrm{i}\phi} & c \\ 0 & 0 & 0 & -s_2 e^{\mathrm{i}\phi} \\ s_2 e^{\mathrm{i}\phi} & c & 0 & 0 \\ 0 & \sqrt{3}s_1 e^{\mathrm{i}\phi} & 0 & 0 \end{pmatrix}. \tag{A·8}$$

In the matrix elements, c, s_1, and s_2 are given by

$$c = \sqrt{\frac{2}{3}}\cos\theta, \quad s_1 = \frac{1}{\sqrt{2}}\sin\theta, \quad s_2 = \frac{1}{\sqrt{6}}\sin\theta, \tag{A·9}$$

where θ takes arbitrary values as well as ϕ, which are related to the mixing of the local $t_u(x, y, z)$ symmetric orbitals and the $+$ band shown as

$$\langle x|+\rangle : \langle y|+\rangle : \langle z|+\rangle = \sin\theta\cos\phi : \sin\theta\sin\phi : \cos\theta. \tag{A·10}$$

Here, $|+\rangle$ represents a partial wave of the $+$ band electrons with the t_u symmetry at an impurity site. The details of impurity scattering due to such a multipole as the octupole are described for the f^2 singlet-triplet configuration in the previous paper.[7]

In the presence of a magnetic field, the T_η operators are expressed as

$$T_z = \begin{pmatrix} 0 & b & (a_+ - a_-) & -b \\ b & 0 & 0 & 0 \\ (a_+ - a_-) & 0 & 0 & 0 \\ -b & 0 & 0 & 0 \end{pmatrix}, \tag{A·11}$$

$$T_+ = \begin{pmatrix} 0 & \sqrt{2}a_- e^{\mathrm{i}\phi_h} & \sqrt{2}b e^{\mathrm{i}\phi_h} & \sqrt{2}a_+ e^{\mathrm{i}\phi_h} \\ -\sqrt{2}a_+ e^{\mathrm{i}\phi_h} & 0 & 0 & 0 \\ \sqrt{2}b e^{\mathrm{i}\phi_h} & 0 & 0 & 0 \\ -\sqrt{2}a_- e^{\mathrm{i}\phi_h} & 0 & 0 & 0 \end{pmatrix}, \tag{A·12}$$

on the basis of $(\Gamma_1, +, 0, -)$, where $(+, 0, -)$ denote the excited triplet states that satisfy eq. (20). The parameters in each matrix element are magnetic-field-dependent and are defined as

$$a_\pm = \frac{1}{2}(1 \pm \bar{h}_z), \quad b = \frac{1}{\sqrt{2}}\sqrt{\bar{h}_x^2 + \bar{h}_y^2}, \quad \tan\phi_h = \frac{\bar{h}_y}{\bar{h}_x}, \tag{A·13}$$

where $\boldsymbol{h}/h \equiv (\bar{h}_x, \bar{h}_y, \bar{h}_z)$. Equations (A·11) and (A·12) for $\bar{h}_z = 1$ correspond to eqs. (A·5) and (A·6), respectively. Using the matrices in eqs. (A·7) and (A·8) to calculate

$$\langle\Gamma_1|\hat{I}_S|0\rangle = (a_+ - a_-)\hat{t}_z + \frac{1}{\sqrt{2}}b e^{\mathrm{i}\phi_h}\hat{t}_- + \frac{1}{\sqrt{2}}b e^{-\mathrm{i}\phi_h}\hat{t}_+ \tag{A·14}$$

in eq. (23), we obtain

$$C_h = \left(\frac{1}{6} + a_+a_-\right)\sin^2\theta + \left(\frac{2}{3} - 2a_+a_-\right)\cos^2\theta + 2\sqrt{a_+a_-}(a_+ - a_-)\sin\theta\cos\theta\cos(\phi_h - \phi) + (a_+a_-)\sin^2\theta\cos 2(\phi_h - \phi), \tag{A·15}$$

which depends on the details of the hybridization of local f-electron states with the + band represented by θ and ϕ in eq. (A·10). We note the following equality:

$$\sum_{n=0,\pm} \mathrm{Tr}_{\hat{\tau}\hat{\sigma}}\left[\langle\Gamma_1|\hat{I}_S|n\rangle\langle n|\hat{I}_S|\Gamma_1\rangle\right] = 1. \tag{A·16}$$

To compare the magnetic and nonmagnetic exchange properties, we also present the Γ_5-type quadrupole operators

$$Q_z = \begin{pmatrix} 0 & 0 & -\mathrm{i} & 0 \\ 0 & 0 & 0 & 0 \\ \mathrm{i} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \tag{A·17}$$

$$Q_+ = Q_-^\dagger = -\sqrt{2}\begin{pmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \tag{A·18}$$

which correspond to the T_η octupole operators in eqs. (A·5) and (A·6), respectively, and the quadrupolar exchange operators

$$\hat{q}_z = -\frac{1}{2}\begin{pmatrix} 0 & 0 & c & s_2e^{-\mathrm{i}\phi} \\ 0 & 0 & -s_2e^{\mathrm{i}\phi} & c \\ c & -s_2e^{-\mathrm{i}\phi} & 0 & 0 \\ s_2e^{\mathrm{i}\phi} & c & 0 & 0 \end{pmatrix}, \tag{A·19}$$

$$\hat{q}_+ = \hat{q}_-^\dagger = \mathrm{i}\frac{1}{2}\begin{pmatrix} 0 & 0 & \sqrt{3}s_1e^{\mathrm{i}\phi} & -c \\ 0 & 0 & 0 & s_2e^{\mathrm{i}\phi} \\ s_2e^{\mathrm{i}\phi} & c & 0 & 0 \\ 0 & \sqrt{3}s_1e^{\mathrm{i}\phi} & 0 & 0 \end{pmatrix}, \tag{A·20}$$

which correspond to the octupolar exchange operators ($\hat{t}_\eta$) in eqs. (A·7) and (A·8), respectively.[7] Let us take $s_1 = s_2 = 0$ to simplify $\hat{t}_z$ and $\hat{q}_z$ as

$$\hat{t}_z = \frac{c}{2}\begin{pmatrix} 0 & 0 & -\mathrm{i} & 0 \\ 0 & 0 & 0 & -\mathrm{i} \\ \mathrm{i} & 0 & 0 & 0 \\ 0 & \mathrm{i} & 0 & 0 \end{pmatrix},$$

$$\hat{q}_z = -\frac{c}{2}\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}. \tag{A·21}$$

They express the spin-independent scattering with only orbital exchange. In the band space, it is clear that the former $\hat{\tau}_2$ type is magnetic and the latter $\hat{\tau}_1$ type is nonmagnetic.[7] It is easy to check whether the effective paring interaction mediated by such impurity scattering is attractive or repulsive in the $s_\pm$-wave state as follows.

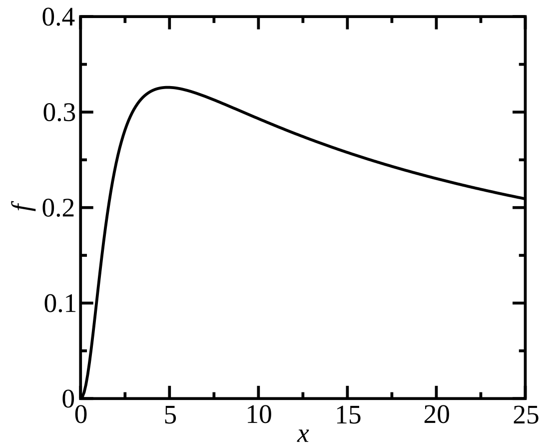

Fig. B·1. Plot of $f(x)$.

Since the $s_\pm$-wave state is expressed by $\Delta\hat{\tau}_3\hat{\rho}_2\hat{\sigma}_2$ in the $\hat{\tau}\otimes\hat{\rho}\otimes\hat{\sigma}$ space, the $\hat{\tau}_2$-type magnetic scattering satisfies

$$\hat{\tau}_2(\Delta\hat{\tau}_3\hat{\rho}_2\hat{\sigma}_2)\hat{\tau}_2 = -\Delta\hat{\tau}_3\hat{\rho}_2\hat{\sigma}_2, \tag{A·22}$$

which is used for deriving f_Δ in eq. (13). The sign reversal of Δ indicates that the impurity-mediated pairing interaction is attractive. On the contrary, it becomes repulsive for the $\hat{\tau}_1$-type nonmagnetic scattering since

$$\hat{\tau}_1\hat{\rho}_3(\Delta\hat{\tau}_3\hat{\rho}_2\hat{\sigma}_2)\hat{\tau}_1\hat{\rho}_3 = \Delta\hat{\tau}_3\hat{\rho}_2\hat{\sigma}_2 \tag{A·23}$$

results in the absence of sign reversal of Δ owing to $\hat{\rho}_3$ in the particle-hole space that accompanies the nonmagnetic scattering. In a similar analysis, one can confirm that the nonmagnetic (magnetic) scattering leads to the attractive (repulsive) interaction effectively for the s_{++}-wave pairing. Therefore, T_c can be increased by either the magnetic scattering in the $s_\pm$-wave state or the nonmagnetic scattering in the s_{++}-wave state in the case of interband impurity scattering with the a_u-t_u orbital exchange.

Appendix B: Function as the Impurity Effect on T_c

Each gap equation presented in this paper gives the level-splitting x-dependent T_c determined by $f(x) = -f_\Delta(x) + f_\omega(x)$ that is defined in eq. (16). For the calculation of $f(x)$ plotted in Fig. B·1, the necessary formulas are arranged here:[7,8]

$$f_\Delta(x) = -\frac{\tanh x}{x} + A(x) - \frac{1}{2}B(x),$$

$$f_\omega(x) = -1 + \tanh^2 x - \frac{1}{2}B(x), \tag{B·1}$$

where $A(x) \equiv S_1(x)\tanh x$ and $B(x) \equiv S_2(x)\tanh x$ are derived from the following equations as

$$S_1(x) = \frac{4x}{\pi^4}\mathrm{Re}\sum_{n=0}^{\infty}\frac{\psi\left(1+n-\mathrm{i}\frac{x}{\pi}\right) - \psi\left(\frac{1}{2}\right)}{\left(n+\frac{1}{2}\right)\left(n+\frac{1}{2}-\mathrm{i}\frac{x}{\pi}\right)^2},$$

$$S_2(x) = \frac{8}{\pi^3}\mathrm{Im}\sum_{n=0}^{\infty}\frac{\psi\left(1+n-\mathrm{i}\dfrac{x}{\pi}\right)-\psi\left(\dfrac{1}{2}\right)}{\left(n+\dfrac{1}{2}-\mathrm{i}\dfrac{x}{\pi}\right)^2}, \quad \text{(B·2)}$$

and ψ represents the digamma function.

Appendix C: Multipolar Scattering Anisotropy in a Magnetic Field

It is convenient to divide $F_{\xi,\alpha}$ in eq. (29) into the $\bar{h}_z$-independent term

$$F_\xi(x_0, x_h) = \frac{1}{3}\left[f_\xi(x_0) + f_\xi(x_+) + f_\xi(x_-)\right] \quad \text{(C·1)}$$

and the $\bar{h}_z$-dependent term

$$\eta_\xi(x_0, x_h) = -\frac{1}{8}\left(\frac{1}{3} - \bar{h}_z^2\right)\left[2f_\xi(x_0) - f_\xi(x_+) - f_\xi(x_-)\right], \quad \text{(C·2)}$$

so that $F_{\xi,\alpha}$ is rewritten as

$$F_{\xi,x} = F_{\xi,y} = F_\xi(x_0, x_h) - \eta_\xi(x_0, x_h), \quad \text{(C·3)}$$

$$F_{\xi,z} = F_\xi(x_0, x_h) + 2\eta_\xi(x_0, x_h). \quad \text{(C·4)}$$

The z component of the field $\bar{h}_z$ ($0 \le \bar{h}_z \le 1$) represents a field direction: [110] ($\bar{h}_z = 0$), [001] ($\bar{h}_z = 1$), and [111] ($\bar{h}_z = 1/\sqrt{3}$). One can see that T_c has a field orientation $\bar{h}_z$ dependence, which comes from eq. (C·2). For $x_h \ll 1$, it is reduced to

$$\eta_\xi(x_0, x_h) = \frac{1}{8}\left(\frac{1}{3} - \bar{h}_z^2\right) f''_\xi(x_0) x_h^2, \quad \text{(C·5)}$$

where f'' indicates the second derivative.

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